

HYGROSCOPIC ACRYLIC FIBER HAVING PH BUFFERING PROPERTY AND ITS PRODUCTION

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Inventor(s): WAKITANI MITSURU; NAKAJIMA SHIGERU; YAMAMOTO YOKO

Applicant(s): JAPAN EXLAN CO LTD

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Abstract

PURPOSE: To obtain a hygroscopic acrylic fiber having larger buffering ability of weakly acidic pH and durability and having 15-35% moisture absorption under 20 deg.C 65% RH and having multifunctions of flame resistance, antimicrobial property, antistatic performance and pill resistance.

CONSTITUTION: This acrylic fiber is a crosslinked acrylic fiber having 1.0-8.0wt.% increase of nitrogen content due to hydrazine crosslinkage and in the fiber, 2. 5-4.5meq/g carboxyl group is introduced in a part of residual nitrile group and an amide group is introduced in the residual part and a part of the carboxyl group is a metal salt type obtained by adding one or two or more kinds of metal salts selected from nitrate, hydrochloride, sulfate and phosphate of Ca, Mg and Al at pH4.0-7.0 to the group and converting the group and the equivalent ratio (metal/H) is in the range of (1.0/1.5) to (4.0/1.0).

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$$\text{N} \quad \frac{1,000}{1-1} - \frac{8,000}{14} \text{ mm min/g}$$
$$0.7 - 5.7 \text{ mm min}$$
$$\approx 0.42.0$$

$$\text{CO}_2\text{H} \quad 2.5 - 4.5 \text{ g-}$$
$$0.6 - 4.0$$

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(71) Applicant: **JAPAN EXLAN CO LTD**

(72) Inventor: **WAKITANI MITSURU**
NAKAJIMA SHIGERU
YAMAMOTO YOKO

(54) **HYGROSCOPIC ACRYLIC FIBER HAVING PH BUFFERING PROPERTY AND ITS PRODUCTION**

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(71)出願人 000004053
日本エクスラン工業株式会社
大阪府大阪市北区堂島浜2丁目2番8号
(72)発明者 脇谷 満
岡山県岡山市海吉2148-10
(72)発明者 中島 茂
岡山県岡山市西大寺中野490番地の8
(72)発明者 山本 葉子
岡山県岡山市金岡東町3丁目1番10号
(74)代理人 弁理士 安達 光雄 (外2名)

(54)【発明の名称】 pH緩衝性吸湿性アクリル系繊維及びその製造方法

(57)【要約】

【目的】 弱酸性のpH緩衝能力が大きく耐久性があり、且つ20°C 65%RH下で15~35%の吸湿率を有し、その上難燃性、抗菌性、制電性、抗ピル性の多機能を有するpH緩衝性吸湿性アクリル系繊維を提供する。

【構成】 ヒドラジン架橋による窒素含有量の増加が1.0~8.0重量%である架橋アクリル系繊維であって、残存ニトリル基の一部には2.5~4.5meq/gのカルボキシル基が、残部にはアミド基が導入されており、該カルボキシル基の一部がpH4.0~7.0においてCa, Mg, Alの硝酸塩、塩酸塩、硫酸塩、磷酸塩より選ばれた1種又は2種以上の金属塩を添加して変換した金属塩型であり、且つその当量比(金属対H)が1.0対1.5から4.0対1.0の範囲にあることを特徴とするpH緩衝性吸湿性アクリル系繊維。

【特許請求の範囲】

【請求項1】 ヒドラジン架橋による窒素含有量の増加が1.0~8.0重量%である架橋アクリル系繊維であって、残存ニトリル基の一部には2.5~4.5 meq/gのカルボキシル基が、残部にはアミド基が導入されており、該カルボキシル基の一部がpH 4.0~7.0においてCa, Mg, Alの硝酸塩、塩酸塩、硫酸塩、磷酸塩より選ばれた1種又は2種以上の金属塩を添加して変換した金属塩型であり、且つその当量比（金属対H）が1.0対1.5から4.0対1.0の範囲にあることを特徴とするpH緩衝性吸湿性アクリル系繊維。

【請求項2】 アクリル系繊維にヒドラジン処理により架橋結合を導入して窒素含有量の増加を1.0~8.0重量%の範囲内に調整し、加水分解反応により残存しているニトリル基量の2.5~4.5 meq/gにカルボキシル基を、残部にアミド基を導入し、酸加水分解のときは、Li, Na, Kより選ばれた1種又は2種以上の水酸化物で、アルカリ加水分解のときは、硫酸、塩酸、硝酸および磷酸より選ばれた1種又は2種以上の酸でpH 4.0~7.0に調整してカルボキシル基の一部を塩型にした後、必須成分としてのCa, Mg, Alの硝酸塩、塩酸塩、硫酸塩、磷酸塩より選ばれた1種又は2種以上の金属塩を添加して一部を金属塩型に変換することを特徴とするpH緩衝性吸湿性アクリル系繊維の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】 本発明は繊維に接触する水のpHをpH 5~7の弱酸性（以下単に弱酸性という）に保持する機能を有し、且つ20°C 65%RH下で15~35%の吸湿率を有するpH緩衝性吸湿性アクリル系繊維及びその製造方法に関する。

【0002】

【従来の技術】 人の皮膚は正常な状態では、分泌される乳酸等によって弱酸性に保たれているが、近年の環境破壊に伴う酸性雨や、洗濯による衣服のアルカリ化によって皮膚のpHが正常な範囲をこえ、これが健康な肌をそこなっている。肌のpHを弱酸性に保つためには外部からの酸やアルカリを衣服によって中和すると共に、肌に接触する繊維素材そのものが弱酸性であることが望ましい。この様な要望に答える方法として、弱酸性に等電点を持つタンパク質を繊維製品への後加工によって付着させたものがある。しかし、この方法はpH緩衝性物質を後加工によって繊維製品に付着させているため、各種の形態に容易に加工できない欠点を有するものであり、又最近社会的ニーズとして高まりつつある吸湿性、難燃性、抗菌性、制電性、抗ピル性の要求を満たすものではなかった。

【0003】

【発明が解決しようとする課題】 本発明者は、このよう

な従来技術の問題点を解消するために、特願平6-36597でアクリル系繊維をヒドラジン処理により架橋し、次いで加水分解処理を施し、生成したカルボキシル基を酸型に変換後、金属水酸化物でその一部を金属塩型に変換することを特徴とするpH緩衝性繊維およびその製造方法を提案したが、カルボキシル基が酸型の場合は繊維の膨潤が小さく金属塩型に変換する際、内部迄均一に反応しにくいことから金属水酸化物添加量を少量づつ添加する必要があり、工業的に製造する上で時間が多大にかかること、表層部に金属塩が多く分布するためその方法で製造したpH緩衝性繊維を染色加工する際に、特に染液pHの高い染色において金属塩が脱落し染液が汚染し染上がり製品へ粉状に付着する等、耐久性に欠点を持つことが明らかになった。

【0004】 本発明はかかる従来技術の現状に鑑み創案されたものであり、その目的とするところは、弱酸性のpH緩衝能力が大きく耐久性があり、且つ20°C 65%RH下で15~35%の吸湿率を有し、その上難燃性、抗菌性、制電性、抗ピル性の多機能を有するpH緩衝性吸湿性アクリル系繊維およびその工業的に有利な製造方法を提供することにある。

【0005】

【課題を解決するための手段】 本発明者は上記目的を達成するために鋭意検討した結果、本発明の完成に至った。即ち、本発明はヒドラジン架橋による窒素含有量の増加が1.0~8.0重量%である架橋アクリル系繊維であって、残存ニトリル基の一部には2.5~4.5 meq/gのカルボキシル基が、残部にはアミド基が導入されており、該カルボキシル基の一部がpH 4.0~7.0においてCa, Mg, Alの硝酸塩、塩酸塩、硫酸塩、磷酸塩より選ばれた1種又は2種以上の金属塩を添加して変換した金属塩型であり、且つその当量比（金属対H）が1.0対1.5から4.0対1.0の範囲にあることを特徴とするpH緩衝性吸湿性アクリル系繊維である。また、本発明はアクリル系繊維にヒドラジン処理により架橋結合を導入して窒素含有量の増加を1.0~8.0重量%の範囲内に調整し、加水分解反応により残存しているニトリル基量の2.5~4.5 meq/gにカルボキシル基を、残部にアミド基を導入し、酸加水分解のときは、Li, Na, Kより選ばれた1種又は2種以上の水酸化物で、アルカリ加水分解のときは、硫酸、塩酸、硝酸および磷酸より選ばれた1種又は2種以上の酸でpH 4.0~7.0に調整してカルボキシル基の一部を塩型にした後、必須成分としてのCa, Mg, Alの硝酸塩、塩酸塩、硫酸塩、磷酸塩より選ばれた1種又は2種以上の金属塩を添加して一部を金属塩型に変換することを特徴とするpH緩衝性吸湿性アクリル系繊維の製造方法である。

【0006】 以下、本発明を詳述する。まず、本発明の架橋アクリル系繊維は、その出発アクリル系繊維として

アクリロニトリル（以下、ANという）を40重量%以上、好ましくは50重量%以上含有するAN系重合体により形成された繊維であり、短纖維、トウ、糸、編織物、不織布等いずれの形態のものでもよく、また、製造工程途中品、廃繊維などでも構わない。AN系重合体は、AN単独重合体、ANと他のモノマーとの共重合体のいずれでも良く、他のモノマーとしては、ハロゲン化ビニル及びハロゲン化ビニリデン；（メタ）アクリル酸エステル；メタリルスルホン酸、p-スチレンスルホン酸等のスルホン酸含有モノマー及びその塩；（メタ）アクリル酸、イタコン酸等のカルボン酸基含有モノマー及びその塩；アクリルアミド、スチレン、酢酸ビニル等のその他のモノマーが挙げられる。

【0007】該アクリル系繊維にヒドラジン架橋を導入する方法としては、窒素含有量の増加を1.0～8.0重量%に調整しうる手段である限り特に限定されないが、濃度5～80重量%（好ましくは5～40重量%）、温度50～130℃（好ましくは85～130℃）で、1～8時間（好ましくは1～4時間）処理する手段が工業的に好ましい。ここで窒素含有量の増加とは、原料アクリル系繊維の窒素含有量とヒドラジン架橋アクリル系繊維の窒素含有量との差をいう。

【0008】なお、窒素含有量の増加が上記下限に満たない場合には、最終的に実用上満足し得る物性の繊維が得られず、その上難燃性、抗菌性、制電性、抗ピル性の多機能が得られず、上限を越えると吸湿性、pH緩衝性が得られず、いずれも発明の目的が達成されない。ここで採用し得るヒドラジンとしては、水加ヒドラジン、硫酸ヒドラジン、塩酸ヒドラジン、硝酸ヒドラジン、臭素酸ヒドラジン等が例示される。

【0009】また、加水分解反応により、ヒドラジン架橋されずに残存しているニトリル基を実質的に消失させ、最終的に2.5～4.5 meq/gのカルボキシル基と残部にアミド基を導入する方法としては、アルカリ金属水酸化物、アンモニア等の塩基性水溶液、或いは硝酸、硫酸、塩酸等の鉱酸の水溶液を含浸、または該水溶液中に原料繊維を浸漬した状態で加熱処理する手段が挙げられる。なお、前記架橋結合の導入と同時に加水分解反応を行うこともできる。ここにおいて、最終的にカルボキシル基量が上記下限に満たない場合には、実用上満足し得るpH緩衝能が得られず、さらに20℃65%RH下で15～40%の吸湿率が得られず、その上難燃性、抗菌性、制電性、抗ピル性の多機能が得られない。また上限を越えると実用上満足しうる物性の繊維が得られない。

【0010】かくして導入されたカルボキシル基を必須成分としてのCa、Mg、Alから選ばれた1種又は2種以上の金属とHとの当量比（金属対H）を1.0対1.5から4.0対1.0に調整する方法としては、上述した加水分解を酸で行った時は、Li、Na、Kより

選ばれた1種又は2種以上の水酸化物で、アルカリ加水分解のときは、硫酸、塩酸、硝酸および磷酸より選ばれた1種又は2種以上の酸でpH4.0～7.0に調整してカルボキシル基の一部を塩型に変換し、必須成分としてのCa、Mg、Alの硝酸塩、塩酸塩、磷酸塩より選ばれた1種又は2種以上の金属塩を添加してカルボキシル基の一部を金属塩に変換し、かかる後水洗、油剤処理、乾燥する方法が用いられる。ここで使用する水酸化物、鉱酸及び金属塩は水に対する溶解度が高く、又pHを4.0～7.0に調整することにより、カルボキシル基の一部が解離状態になり、かくして処理される繊維の微細構造が半膨潤し、金属塩への変換が繊維内部まで均一に且つ素速く行われる。この方法によってはじめて工業的に有利にpH緩衝性吸湿性繊維を製造することが可能になり、且つ染色、洗濯に対して金属塩の脱落が防止できるのである。

【0011】なおCa、Mg、Al以外の金属塩型カルボキシル基ではpHを弱酸性に緩衝できないか、人体に対する有害性が懸念されることから推奨できない。例えばNa、K、Li等のアルカリ金属塩型は、酸に対するpH緩衝能は有するが、アルカリに対する緩衝能力が劣る。これを避けるためにH型比を大きくすると酸に対する緩衝性が低下し、実質的に弱酸性に緩衝能を有するpH緩衝性繊維ではなくなる。次にCa、Mg、Al金属塩型カルボキシル基とH型カルボキシル基の比が1.0対1.5に満たない場合には酸に対する緩衝性が少なく、4.0対1.0を越える場合にはアルカリに対する緩衝性が少なく実用上弱酸性に緩衝能を有するpH緩衝性繊維ではなくなり、いずれも発明の目的を達成できない。なお、本発明では金属塩の種類としてCa、Mg、Alのいずれかが採用されることが必須であるが、pH緩衝性、難燃性、抗菌性、制電性、抗ピル性及び20℃65%RH下で15～35%の吸湿率を損なわない範囲でこれら以外の金属を使用することもできる。しかしその含有量は、金属塩型カルボキシル基として0.4 meq/g以下である。

【0012】このようにして、1g/dの引張強度以上でpH緩衝性のある難燃性、抗菌性、制電性、抗ピル性及び20℃65%RH下で15～35%の吸湿率を兼備するアクリル系繊維を工業的に有利に提供することができる。かくして製造される本発明の繊維は、ニトリル基が大きく変性されているのでアクリル変性繊維と称することもできるものである。尚、特に高い引張強度を求める場合には、後述するように出発アクリル系繊維として二色性比の高い繊維を選ぶのが良い。

【0013】上記アクリル系繊維を製造するための装置としては、アクリル系繊維をポンプ循環系を備えた容器内に充填し、上記架橋結合の導入、加水分解反応、及び金属塩の形成の各反応を逐次行う手段が、安全性、均一反応性等の諸点から望ましい。かかる装置（ポンプ循環

系を備えた容器) の代表例としては、加圧型オーバーマイヤー染色機等が挙げられる。

【0014】また、実用上問題のない繊維物性とpH緩衝性、難燃性、抗菌性、抗ピル性、制電性及び20°C 65%RH下で15~35%の吸湿率を兼ね備えた繊維を提供するためには、特に下記特性を備えた出発アクリル系繊維を採用することが望ましい。

【0015】即ち、繊維を形成するAN系重合体分子が十分に配向しておりコンゴーレッド(以下CRという)二色性比が0.4以上、更に好ましくは0.5以上のアクリル系繊維を採択することが望ましい。なお、CR二色性比は、高分子化学23(252)193(1966)記載の方法に従って求められるものである。

【0016】なお、かかるアクリル系繊維の製造手段に限定ではなく、上記CR二色性比が満たされる限り、適宜公知の手段を用いることができるが、中でも全延伸倍率を4倍以上、好ましくは8倍以上とし、かつ工程収縮率を40%以下、好ましくは30%以下とする手段の採用により工業的に有利に所望のアクリル系繊維を製造することができる。

【0017】更に出発アクリル系繊維として、延伸後熱処理前の繊維(AN系重合体の紡糸原液を常法に従って紡糸し、延伸配向されてはいるが、乾燥緻密化、湿熱緩和処理等の熱処理の施されていない繊維、中でも湿式又は乾/湿式紡糸、延伸後の水膨潤ゲル状繊維:水膨潤度は30~150%)を使用することにより、反応液中への繊維の分散性、繊維中の反応液の浸透性などが改善され、以て架橋結合の導入や加水分解反応が均一かつ速やかに行われる所以望ましい。なお、水膨潤度とは乾燥繊維重量基準で表した含有水分量の百分率である。

【0018】

【作用】本発明に係るpH緩衝性吸湿性アクリル系繊維及びその製造方法が難燃性、抗菌性、抗ピル性、制電性及び20°C 65%RH下で15~35%の吸湿率を兼ね備える理由は、十分に解明するに至っていないが、概ね次のように考えられる。

【0019】即ち、本発明に係る繊維は、AN系重合体

から出発しているところから、ポリマー鎖に結合している側鎖は、ヒドラジンとの反応により生成した窒素を含有する架橋構造と、ニトリル基の加水分解反応により生成したH型、金属塩型カルボキシル基及びアミド基と考えられる。

【0020】一般に塩型カルボキシル基はpH緩衝性を有するが、本発明においてCa、Mg、Alの金属塩型とH型との特定比率のカルボキシル基が弱酸性に緩衝性を示すのは、弱塩基の金属塩と弱酸が適度に共存するためであろう。難燃性は架橋構造とアクリルアミド及びカルボン酸の金属塩により、抗菌性は架橋構造によりもたらされているものと推定する。又、制電性は高吸湿水分による漏洩効果により、抗ピル性は低強度により、更に高吸湿性は架橋構造と金属塩型カルボキシル基によるものであろう。また加工性能を支えているのは、CR二色性比にみられる配向構造と多価金属による分子内、分子間のイオン架橋に由来するところが大であろう。

【0021】

【実施例】以下本発明を実施例により具体的に説明するが、本発明はこれらに限定されるものではない。実施例中の部及び百分率は断りのない限り重量基準で示す。

【0022】なお、pH緩衝能力($\mu\text{eq/g}$)、全カルボキシル基量、金属塩型カルボキシル基量、H型カルボキシル基量(meq/g)、LOI(限界酸素指数)、吸湿率、抗菌性(増減値差)、抗ピル性(ICI等級)及び制電性(半減期)は以下の方法により求めた。

【0023】(1) pH緩衝能力($\mu\text{eq/g}$)

十分乾燥した供試繊維約0.4gを精秤し(X)g、これに200mlの水を加えた後、0.1N塩酸水溶液あるいは0.1N苛性ソーダ水溶液を滴下し、塩酸水溶液の場合はpH5.0になるまでに、また苛性ソーダ水溶液の場合はpH7.0になるまでに消費された塩酸水溶液または苛性ソーダ水溶液消費量(Y)ccを求め、次式によって、酸またはアルカリに対する緩衝能力を算出した。

$$\text{pH緩衝能力}(\mu\text{eq/g}) = \frac{1000Y}{X}$$

【0024】(2) 全カルボキシル基量(meq/g)

十分乾燥した供試繊維約1gを精秤し(X)g、これに200mlの1N塩酸水溶液を加え30分間放置したのちガラスフィルターで濾過し水を加えて水洗する。この塩酸処理を3回繰り返したのち、濾液のpHが5以上に

なるまで十分に水洗する。次にこの試料を200mlの水に入れ1N塩酸水溶液を添加してpH2にした後、0.1N-苛性ソーダ水溶液で常法に従って滴定曲線を求めた。該滴定曲線からカルボキシル基に消費された苛性ソーダ水溶液消費量(Y)ccを求め、次式によって全カルボキシル基量を算出した。

$$0.1Y$$

$$\text{全カルボキシル基量}(\text{meq/g}) = \frac{0.1Y}{X}$$

【0025】(3) 金属塩型カルボキシル基量(meq/g)

十分乾燥した供試繊維を精秤し常法に従って濃硫酸と濃硝酸の混合溶液で酸分解したのち、金属を常法に従って原子吸光光度法により定量し、金属の結合したカルボキシル基量として算出した。

【0026】(4) H型カルボキシル基量 (m eq/g)

次式によりH型カルボキシル基量を算出した。H型カルボキシル基量=全カルボキシル基量-金属塩型カルボキシル基量

【0027】(5) LOI

JIS-7201の最低酸素指数の測定法に従って行なった。

【0028】(6) 吸湿率 (%)

試料繊維約5.0gを熱風乾燥機で105℃、16時間乾燥して重量(W1)gを測定する。次に試料を温度20℃で相対湿度65%に調整された恒温恒湿機に24時間入れて置く。このようにして吸湿した試料の重量(W2)gを測定する。以上の結果から、吸湿率を次式に従って算出した。

$$\text{吸湿率} (\%) = \frac{W2 - W1}{W1} \times 100$$

【0029】(7) 抗菌性

試験菌株: 黄色葡萄球菌 *Staphylococcus aureus* IFO 12732

試験方法: 繊維製品衛生加工協議会(SEK)で定める方法により、滅菌試料布に試験菌のブイヨン懸濁液を注加し、密閉容器中で、37℃、18時間培養後の生菌数を計測し、植菌数Aに対する標準布の菌数Bと試料の菌数Cの増減値差で求める。

増減値 = $\log C - \log A$

増減値差 = $(\log B - \log A) - (\log C - \log A)$

表 1

g A)

【0030】(8) 抗ピル性

JIS-L-1076繊物及び編物のピリング試験方法A法のICI型試験機を用いる方法に従って行った。

【0031】(9) 制電性

JIS-L-1094繊物及び編物の帯電性試験方法に従って行なった。

【0032】実施例 1

AN90%及びアクリル酸メチル(以下、MAという)10%からなるAN系重合体(30℃ジメチルホルムアミド中での極限粘度[η]: 1.2)10部を48%のロダンソーダ水溶液90部に溶解した紡糸原液を、常法に従って紡糸、延伸(全延伸倍率: 10倍)した後、乾球/湿球=120℃/60℃の雰囲気下で乾燥して、次いで125℃の高圧スチーム下で緩和処理(工程収縮率27%)して単繊維織度1.0dの原料繊維(CR二色性比0.56)を得た。

【0033】原料繊維10gを表1に示した条件で1Lのヒドラジン水溶液及び1LのNaOH水溶液で処理した後、水洗した。得られた繊維を表1に記載した条件でpH調整処理をした後水洗しカルボキシル基の一部がH型となった繊維を得た。ヒドラジン処理後の窒素增加量は5.0重量%、加水分解処理後の全カルボキシル量は4.2m eq/gであった。次に得られた繊維を表1に記載した条件で各種の金属塩を加えて金属塩処理を実施した。十分に水洗した後乾燥しpH緩衝性吸湿性繊維No.1~7を得た。このNo.1~7のpH緩衝性吸湿性繊維の特性値を表2に示した。

【0034】

【表1】

例	繊維 No.	ヒドラジン処理			NaOH処理			pH調整処理		金属塩処理			
		%	℃	HR	%	℃	HR	酸種類	pH	種類	℃	HR	調整pH
本発明例	1	35	98	2	10	90	2	HNO ₃	6.5	Ca(NO ₃) ₂	60	2	なりゆき
本発明例	2	10	120	3	10	90	2	HNO ₃	6.0	Ca(NO ₃) ₂	60	2	なりゆき
本発明例	3	5	125	5	10	90	2	HNO ₃	5.5	Ca(NO ₃) ₂	60	2	なりゆき
本発明例	4	22	98	5	10	90	2	HCl	6.0	CaCl ₂	60	2	なりゆき
本発明例	5	22	98	3	10	90	2	H ₂ SO ₄	6.0	CaCl ₂	60	2	なりゆき
比較例	6	22	98	5	10	90	2	HCl	0	Ca(OH) ₂	60	5	6.0
比較例	7	22	98	5	10	90	2	HCl	0	Ca(OH) ₂	60	24	6.0

【0035】

【表2】

表 2

例 No.	織維 C a型/H型 カルボキシル基 当量比	pH緩衝能力 (μeq/g) 酸 アルカリ	引張強度 g/d	難燃性 LOI (%)	抗菌性 S E K 菌数増減値差	20°C 65%RH 吸湿率 (%)
本発明例 1	3.9/1	1300 300	17	29	2.2	30
本発明例 2	2.5/1	1000 320	18	28	2.3	28
本発明例 3	1.6/1	700 600	20	26	1.8	25
本発明例 4	2.7/1	1000 350	16	28	2.4	27
本発明例 5	2.4/1	1000 330	18	28	2.1	26
比較例 6	2.3/1	610 320	14	28	2.0	22
比較例 7	2.5/1	700 300	15	29	2.1	24

【0036】表1及び表2からわかるように、本発明例のpH緩衝性吸湿性繊維No. 1～5は、本発明者が先に提案した比較例No. 6～7に比べてpH調整及び金属塩処理時間を大幅に短縮したにもかかわらず、引張強度、難燃性、抗菌性、吸湿率のいずれの特性値も勝るとも劣らない優れた性能を得ることができる。

【0037】実施例 2

実施例1で作成した、本発明例（繊維No. 1、No. 4）及び比較例（繊維No. 6）の3種のpH緩衝性吸湿性繊維に油剤処理、乾燥処理を行い、1.8デニール

表 3

×48mmの製品原綿を得た。これらの製品原綿を常法に従って、混綿、カード、練条、粗紡、精紡を行い、1/52メートル番手、撚り数830T/Mの糸を作成した。次に、これらの糸を20ゲージのスムース編機で目付が200±20g/m²の、表3に示すAからFの編地サンプルを作成した。次いで、これらのサンプル編地をH₂O₂/NaOH (pH=9、80°C×60分)で晒染色を実施した。

【0038】

【表3】

例	混紡率%	編地 サンプル No.	紡績加工 白粉発生	晒染色 染液濁り
本発明例	繊維 No.1/A n=100/0	A	認めず	極僅か
本発明例	繊維 No.4/A n=100/0	B	認めず	極僅か
本発明例	繊維 No.1/A n=30/70	C	認めず	認めず
本発明例	繊維 No.4/C o=30/70	D	認めず	認めず
比較例	繊維 No.6/A n=100/0	E	あり	多い
比較例	繊維 No.6/A n=30/70	F	少しあり	やや多い

A n: アクリル繊維エクスラン K8-1.5 d×51mm

C o: 木綿 コーマ

【0039】本発明例（繊維No. 1、No. 4）は、紡績、編み、染色いずれの工程でも、加工上何らの問題もなかったが、比較例（繊維No. 6）は、カード工程及び精紡工程で白粉が認められ、更に晒染色残浴の濁りが多く認められた。これは、pH調整及び金属水酸化物処理に時間を掛けたにかかわらず、未反応の水酸化カルシウムが繊維表面及び繊維内部に残存したためと考える。

【0040】晒染色後のサンプル編地A～Fの吸湿率、

抗菌性、制電性、抗ピル性試験の結果を表4に示す。本発明例のサンプル編地A～Bはいずれも優れた特性を示し、30%混のサンプル編地C～Dに於いても、実用効果が十分な特性を示すことがわかる。これは、金属塩処理が、pH 4.0～7.0に調整してカルボキシル基の一部を塩型にした後、金属塩処理することで、繊維内部迄均一に反応し耐久性が著しく向上したためであろう。比較例のサンプル編地E～Fに於いても、本発明者が目標とする実用性能は維持しているが、加工面で制約があ

る点が問題である。

【0041】

表 4

例	編地 サンプル No.	抗 菌 性 S E K 菌数増減値差	20°C 65%RH 吸湿率 (%)	20°C 40%RH 半減期 (秒)	IC1 5Hr 抗ピル性 (級)
本発明例	A	2. 1	31. 2	1. 0	5
本発明例	B	2. 2	27. 6	1. 3	5
本発明例	C	1. 9	10. 2	12	3
本発明例	D	1. 8	8. 7	14	3
比較例	E	2. 0	25. 9	2. 2	5
比較例	F	1. 8	7. 9	18	3. 5

【0042】

【発明の効果】本発明により、実用上問題のない繊維物性を維持し、20°C×65%RH下での飽和吸湿率が15～35%を有し、且つ難燃性、抗菌性、制電性、抗ピル性を兼ね備えたpH緩衝性吸湿性アクリル系繊維並びに該繊維を工業的に有利に製造する手段を提供することができる。本発明のpH緩衝性吸湿性アクリル系繊維はそれ自体が弱酸性にあり、外界からの酸、アルカリの攻撃にもpH5～7の範囲内に維持する能力に優れる。また

具体的には、LOI表示で24以上もの難燃性を示し、抗菌性はS E K菌数増減値差で基準値1. 6を上回り、抗ピル性はIC1法で30%混の編地において3級を上回り、制電性は20°C×40%RH下の半減期が30%混の編地において15秒を下回るという、従来の合成繊維や天然繊維と比べ顕著な諸性能を有する。さらに、不織布、編物、織物などさまざまな形態に加工し得るため、衣料分野をはじめ生活資材や産業資材などあらゆる用途分野に広く用いられる。

* NOTICES *

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1. This document has been translated by computer. So the translation may not reflect the original precisely.
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CLAIMS

[Claim(s)]

[Claim 1] It is the bridge formation acrylic fiber whose increase in the nitrogen content by hydrazine bridge formation is 1.0 - 8.0 % of the weight. To a part of residual nitrile group, the carboxyl group of 2.5 - 4.5 meq/g The amide group is introduced into the remainder and a part of this carboxyl group sets to pH 4.0-7.0. The nitrate of calcium, Mg, and aluminum, pH buffer nature hygroscopicity acrylic fiber which is the metal salt type which added and changed one sort or two sorts or more of metal salts chosen from a hydrochloride, a sulfate, and phosphate, and is characterized by the equivalent ratio (metal pair H) being in the range of 1.0 to 1.5 to 4.0 to 1.0.

[Claim 2] Introduce a crosslinking bond into an acrylic fiber by hydrazine processing, and the increase in a nitrogen content is adjusted to 1.0 - 8.0% of the weight of within the limits. A carboxyl group is introduced into 2.5 - 4.5 meq/g of the amount of nitrile groups which remains by the adding-water decomposition reaction, and an amide group is introduced into the remainder. at the time of acidolysis At the time of alkali hydrolysis with one sort or two sorts or more of hydroxides chosen from Li, Na, and K After one sort or two sorts or more of acids chosen from a sulfuric acid, a hydrochloric acid, a nitric acid, and phosphoric acid adjusting to pH 4.0-7.0 and using a part of carboxyl group as a salt type, The manufacture method of pH buffer nature hygroscopicity acrylic fiber characterized by adding one sort or two sorts or more of metal salts chosen from the nitrate of calcium, Mg, and aluminum as an indispensable component, a hydrochloride, a sulfate, and phosphate, and changing a part into a metal salt type.

[Translation done.]

thing of which form is sufficient as a staple fiber, a tow, thread, a knit fabric, a nonwoven fabric, etc., and the bridge formation acrylic fiber of this invention may also be elegance and a waste fiber in the middle of a manufacturing process. Any of AN homopolymer and the copolymer of AN and other monomers are sufficient as AN system polymer, and the monomer of others, such as carboxylic-acid machine content monomers, such as sulfonic-acid content monomers, such as a halogenation vinyl and a halogenation vinylidene; (meta) acrylic-ester; metallyl sulfonic acid, and p-styrene sulfonic acid, and a salt; (meta) acrylic acid of those, and an itaconic acid, and a salt; acrylamide of those, styrene, and vinyl acetate, is mentioned as other monomers.

[0007] Although it is not limited especially as long as it is a means by which the increase in a nitrogen content can be adjusted to 1.0 - 8.0% of the weight, as a method of introducing hydrazine bridge formation into this acrylic fiber, the means which is 50-130 degrees C (preferably 85-130 degrees C) in 5 - 80 % of the weight (preferably 5 - 40 % of the weight) of concentration and temperature, and carries out processing for 1 to 8 hours (preferably 1 - 4 hours) is industrially desirable. The increase in a nitrogen content means the difference of the nitrogen content of a raw material acrylic fiber, and the nitrogen content of a hydrazine bridge formation acrylic fiber here.

[0008] In addition, when the increase in a nitrogen content does not fulfill the above-mentioned minimum, if the fiber of the physical properties which may finally be satisfied practically is not obtained, and various functions of the upper fire retardancy, antibacterial, an antielectricity characteristic, and anti-pill nature are not obtained but an upper limit is exceeded, hygroscopicity and pH buffer nature will not be obtained and the purpose of invention of all will not be attained. As a hydrazine which can be adopted here, a hydration hydrazine, hydrazine sulfate, a hydrazine hydrochloride, a nitric-acid hydrazine, a bromic-acid hydrazine, etc. are illustrated.

[0009] Moreover, the nitrile group which remains by the adding-water decomposition reaction, without carrying out hydrazine bridge formation is vanished substantially, and a means to heat-treat the solution of mineral acids, such as basic solution, such as an alkali-metal hydroxide and ammonia, or a nitric acid, a sulfuric acid, and a hydrochloric acid, in sinking in or the state where raw material fiber was immersed into this solution, as a method of finally introducing an amide group into the carboxyl group and the remainder of 2.5 - 4.5 meq/g is mentioned. In addition, a adding-water decomposition reaction can also be performed simultaneously with introduction of the aforementioned crosslinking bond. In here, when the amount of carboxyl groups finally does not fulfill the above-mentioned minimum, pH buffer capacity which may be satisfied practically is not obtained, 15 - 40% of moisture absorption is not obtained under 20 more degree-C65%RH, and various functions of the upper fire retardancy, antibacterial, an antielectricity characteristic, and anti-pill nature are not obtained. Moreover, if an upper limit is exceeded, the fiber of the physical properties which may be satisfied practically will not be obtained.

[0010] The carboxyl group introduced in this way calcium as an indispensable component, Mg. As a method of adjusting the equivalent ratio (metal pair H) of one sort or two sorts or more of metals chosen from aluminum, and H to 4.0 to 1.0 from 1.0 to 1.5. When an acid performs hydrolysis mentioned above, they are one sort or two sorts or more of hydroxides chosen from Li, Na, and K. at the time of alkali hydrolysis One sort or two sorts or more of acids chosen from a sulfuric acid, a hydrochloric acid, a nitric acid, and phosphoric acid adjust to pH 4.0-7.0, and a part of carboxyl group is changed into a salt type. One sort or two sorts or more of metal salts chosen from the nitrate of calcium, Mg, and aluminum as an indispensable component, a hydrochloride, and phosphate are added, a part of carboxyl group is changed into a metal salt, and rinsing and the method of oily-medicine-processing and drying are used after an appropriate time. the fine structure of the fiber processed in this way by the hydroxide, mineral acid, and metal salt which are used here having the high solubility to water, and a part of carboxyl group being in a dissociation state by adjusting pH to 4.0-7.0 -- half-- swelling -- conversion in a metal salt -- up to the interior of fiber -- homogeneity -- and base -- it is carried out quickly It becomes possible to manufacture pH buffer nature hygroscopicity fiber advantageously industrially for the first time by this method, and omission of a metal salt can be prevented to dyeing and wash.

[0011] In addition, in calcium, Mg, and metal salt type carboxyl groups other than aluminum, it cannot recommend from we being unable to buffer pH to weak-acid nature, or being anxious about the detrimental nature to a human body. For example, although pH buffer capacity to an acid has alkali-metal salt types, such as Na, K, and Li, they are inferior in the buffer capacity to alkali. It is no longer pH buffer nature fiber which the buffer nature to an acid will fall if H type ratio is enlarged in order to avoid this, and has buffer capacity to weak-acid nature substantially. Next, when the ratio of calcium, Mg, aluminum metal salt type carboxyl group, and H type carboxyl group does not fulfill 1.0 to 1.5, there is little buffer nature to an acid, when exceeding 4.0 to 1.0, the buffer nature to alkali is no longer pH buffer nature fiber which has buffer capacity to weak-acid nature practically few, and neither can attain the purpose of invention. In addition, by this invention, although it is indispensable that calcium, Mg, or aluminum is adopted as a kind of metal salt, metals other than these can also be used in the range which does not spoil 15 - 35% of moisture absorption under pH buffer nature, fire retardancy, antibacterial, an antielectricity characteristic, anti-pill nature, and 20-degree-C65%RH. However, the content is 0.4 or less meq/g as a metal salt type carboxyl group.

[0012] Thus, the acrylic fiber which has 15 - 35% of moisture absorption under the fire retardancy which has pH buffer nature above the tensile strength of 1 g/d, antibacterial, an antielectricity characteristic, anti-pill nature, and 20-degree-C65%RH can be offered advantageously industrially. Since the nitrile group is denaturalizing greatly the fiber of this invention manufactured in this way, it can also be called acrylic denaturation fiber. In addition, when asking for high tensile strength especially, it is good to choose the high fiber of a dichroism ratio as a start acrylic fiber so that it may mention later.

[0013] A means for it to be filled up with an acrylic fiber in the container equipped with the pump circulation system as equipment for manufacturing the above-mentioned acrylic fiber, and to perform serially each reaction of introduction of the above-mentioned crosslinking bond, a adding-water decomposition reaction, and a metal salt of formation is desirable from many points, such as safety and homogeneous-reaction nature. As an example of representation of this equipment (container equipped with the pump circulation system), a pressurized type exaggerated Mayer dyeing machine etc. is mentioned.

[0014] Moreover, especially in order to offer the fiber which has 15 - 35% of moisture absorption under the fiber physical properties which are satisfactory practically, pH buffer nature and fire retardancy, antibacterial, anti-pill nature, an antielectricity characteristic, and 20-degree-C65%RH, it is desirable to adopt the start acrylic fiber equipped with the following property.

[0015] That is, it is desirable for AN system polymer molecule which forms fiber to fully carry out orientation, and for a Congo-Red (for it to be called Following CR) dichroism ratio to adopt 0.5 or more acrylic fibers still more preferably 0.4 or more.

·In addition, CR dichroism ratio is called for according to the method of polymer-chemistry 23 (252) 193 (1966) publication.

[0016] In addition, although a well-known means can be suitably used as long as there is no limitation in the manufacture means of this acrylic fiber and the above-mentioned CR dichroism ratio is filled, a desired acrylic fiber can be industrially manufactured advantageously by adoption of the means which makes all draw magnification 8 or more times preferably 4 or more times especially, and makes a process contraction 30% or less preferably 40% or less.

[0017] Furthermore, as a start acrylic fiber, it is fiber in front of an extension postheat treatment (according to a conventional method, spinning of the spinning undiluted solution of AN system polymer is carried out, and although extension orientation is carried out). Wet or **/wet spinning, and the water swelling gel fiber:water degree of swelling after extension by using 30 - 150% also in the fiber to which heat treatments, such as formation of dryness precise and wet heat relief processing, are not performed. Since the dispersibility of the fiber to the inside of reaction mixture, the permeability of the reaction mixture to the inside of fiber, etc. are improved, with introduction and the adding-water decomposition reaction of a crosslinking bond are performed uniformly and promptly, it is desirable. In addition, a water degree of swelling is the percentage of the content moisture content expressed with dryness fiber weight criteria.

[0018]

[Function] The reason pH buffer nature hygroscopicity acrylic fiber concerning this invention and its manufacture method have 15 - 35% of moisture absorption under fire retardancy, antibacterial, anti-pill nature, an antielectricity characteristic, and 20-degree-C65%RH is considered in general as follows, although it has fully come to solve.

[0019] That is, while the fiber concerning this invention has left AN system polymer, the side chains combined with the polymer chain are considered to be the structure of cross linkage containing the nitrogen generated by the reaction with a hydrazine, H type generated by the adding-water decomposition reaction of a nitrile group, a metal salt type carboxyl group, and an amide group from the place where the nitrile group has disappeared substantially.

[0020] Probably, in this invention, the carboxyl group of the specific ratio of the metal salt type of calcium, Mg, and aluminum and H type shows buffer nature to weak-acid nature, because the metal salt and weak acid of a weak base live together moderately, although a salt type carboxyl group generally has pH buffer nature. What fire retardancy is brought to with the metal salt of the structure of cross linkage, an acrylamide, and a carboxylic acid, and antibacterial is brought by the structure of cross linkage is presumed. Moreover, in an antielectricity characteristic, anti-pill nature will depend high hygroscopicity on the structure of cross linkage and a metal salt type carboxyl group further with low strength according to the disclosure effect by part for high hygroscopic water. Moreover, the place where supporting processability ability originates in the ion bridge formation between the molecules in the molecule by the oriented structure and polyvalent metal which are seen by CR dichroism ratio is size.

[0021]

[Example] Although an example explains this invention concretely below, this invention is not limited to these. As long as there is no notice, weight criteria show the section and percentage in an example.

[0022] In addition, pH buffer capacity (meeq/g), the total amount of carboxyl groups, the amount of metal salt type carboxyl groups, the amount (meq/g) of H type carboxyl groups, LOI (limiting oxygen index), a moisture absorption, antibacterial (increase-and-decrease difference of a value), anti-pill nature (ICI grade), and the antielectricity characteristic (half-life) were searched for by the following methods.

[0023] (1) pH buffer capacity (meeq/g)

After weighing precisely about 0.4g of sample offering fiber dried enough and adding 200ml water to (X) g and this, until 0.1-N hydrochloric-acid solution or 0.1-N caustic-alkali-of-sodium solution is dropped and it is set to pH 5.0 in the case of hydrochloric-acid solution. The hydrochloric-acid solution consumed by the time it was alike and was set to pH 7.0 in the case of caustic-alkali-of-sodium solution, or caustic-alkali-of-sodium solution (consumption Y) cc was calculated, and the buffer capacity to an acid or alkali was computed by the following formula.

1 0 0 0 Y

$$\text{pH緩衡能力 } (\mu \text{eq/g}) = \frac{1000Y}{X}$$

[0024] (2) The total amount of carboxyl groups (meq/g)

After weighing precisely about 1g of sample offering fiber dried enough, adding 200ml 1-N hydrochloric-acid solution to (X) g and this and leaving it for 30 minutes, it filters by the glass filter, and water is added and rinsed. It fully rinses until pH of filtrate becomes five or more, after repeating this hydrochloric-acid processing 3 times. Next, after having paid this sample to 200ml water, adding 1-N hydrochloric-acid solution and making it pH 2, according to the conventional method, the titration curve was searched for in 0.1N-caustic-alkali-of-sodium solution. Caustic-alkali-of-sodium solution (consumption Y) cc consumed by the carboxyl group from this titration curve was calculated, and the total amount of carboxyl groups was computed by the following formula.

$$\text{全カルボキシル基量 (meq/g)} = \frac{0.1Y}{X}$$

[0025] (3) The amount of metal salt type carboxyl groups (meq/g)

After weighing precisely the sample offering fiber dried enough and carrying out acidolysis by the mixed solution of a concentrated sulfuric acid and concentrated nitric acid according to a conventional method, according to the conventional method, the fixed quantity of the metal was carried out by the atomic-absorption photometry, and it computed as an amount of carboxyl groups which the metal combined.

[0026] (4) The amount of H type carboxyl groups (meq/g)

The amount of H type carboxyl groups was computed by the following formula. The amount of H type carboxyl groups = the total amount of amount of carboxyl groups-metal salt type carboxyl groups. [0027] (5) It carried out according to the measuring method of the minimum oxygen index of LOIJIS-7201.

[0028] (6) Moisture absorption (%)

About 5.0g of 105 degrees C of sample fiber is dried by the hot air drying equipment for 16 hours, and a weight (W1) g is measured. next, the constant temperature adjusted to 65% of relative humidity at the temperature of 20 degrees C in the sample -- it puts into a constant humidity machine for 24 hours, and places Thus, the weight (W2) g of the sample which absorbed moisture is measured. From the above result, the moisture absorption was computed according to the following formula.

$$\text{吸湿率 (\%)} = \frac{W2 - W1}{W1} \times 100$$

[0029] (7) Antibacterial examination strain : yellow staphylococcus Staphylococcus aureus IFO 12732 test methods: By the method of defining in a textiles sanitary finishing conference (SEK), **** bouillon suspension of an examination bacillus on sterilization sample cloth, measure the number of micro organisms after 37 degrees C and 18-hour cultivation in an airtight container, and ask with increase-and-decrease the difference of a value of the number B of bacilli of a standard cloth and the number C of bacilli of a sample to the number A of inoculation.

Increase and decrease of value = logC-logA increase-and-decrease difference [of a value] = (logB-logA) - (logC-logA)

[0030] (8) Anti-pill nature JIS L It carried out according to the method using the ICI type testing machine of the pilling test-method A method of 1076 textiles and knitting.

[0031] (9) Antielectricity characteristic JIS L It carried out according to the electrification nature test method of 1094 textiles and knitting.

[0032] Example According to a conventional method, the spinning undiluted solution which dissolved the AN system polymer ([limiting viscosity eta]:1.2 in inside of 30-degree-C dimethylformamide) 10 section which consists of 1AN90% and 10% (henceforth MA) of methyl acrylates in 48% of rhodan soda water solution 90 section is dried under atmosphere (a dry bulb / wet-bulb =120 degree C / 60 degrees C), after extending (all draw magnification; 10 times), spinning and. Subsequently relief processing (27% of process contractions) was carried out under the 125-degree C high pressure steam, and raw material fiber (CR dichroism ratio 0.56) with a single fiber fineness of 1.0d was obtained.

[0033] It rinsed, after processing in the hydrazine solution of 1L, and the NaOH solution of 1L by the conditions which showed 10g of raw material fiber in Table 1. The fiber from which it rinsed after carrying out pH adjustment processing on the conditions which indicated the obtained fiber to Table 1, and a part of carboxyl group became H type was obtained. The total amount of carboxyls after hydrolysis processing of the nitrogen augend after hydrazine processing was 4.2 meq/g 5.0% of the weight. Next, various kinds of metal salts on the conditions which indicated the obtained fiber to Table 1 were added, and metal salt processing was carried out. After fully rinsing, it dried and pH buffer nature hygroscopicity fiber No.1-7 were obtained. The weighted solidity of this pH buffer nature hygroscopicity fiber of No.1-7 was shown in Table 2.

[0034]

[Table 1]

表 1

例	繊維	ヒドラジン処理			NaOH処理			pH調整処理		金属塩処理			
		%	℃	hr	%	℃	hr	酸種類	pH	種類	℃	hr	調整pH
本発明例	1	35	98	2	10	90	2	HNO ₃	6.5	Ca (NO ₃) ₂	60	2	なりゆき
本発明例	2	10	120	3	10	90	2	HNO ₃	6.0	Ca (NO ₃) ₂	60	2	なりゆき
本発明例	3	5	125	5	10	90	2	HNO ₃	5.5	Ca (NO ₃) ₂	60	2	なりゆき
本発明例	4	22	98	5	10	90	2	HCl	6.0	CaCl ₂	60	2	なりゆき
本発明例	5	22	98	3	10	90	2	H ₂ SO ₄	6.0	CaCl ₂	60	2	なりゆき
比較例	6	22	98	5	10	90	2	HCl	0	Ca (OH) ₂	60	5	6.0
比較例	7	22	98	5	10	90	2	HCl	0	Ca (OH) ₂	60	24	6.0

[0035]

[Table 2]

表 2

例	織維 No.	C型/H型 カルボキシル基 当量比	pH緩衝能力 (μeq/g)	引張強度 g/d	難燃性 LOI (%)	抗菌性 SEK 菌致増殖値差	20°C 65%RH 吸湿率 (%)	
本発明例	1	3.9/1	1300	300	17	29	2.2	30
本発明例	2	2.5/1	1000	320	18	28	2.3	28
本発明例	3	1.6/1	700	600	20	26	1.8	25
本発明例	4	2.7/1	1000	350	16	28	2.4	27
本発明例	5	2.4/1	1000	330	18	28	2.1	26
比較例	6	2.3/1	610	320	14	28	2.0	22
比較例	7	2.5/1	700	300	15	29	2.1	24

[0036] As shown in Table 1 and 2, pH buffer nature hygroscopicity fiber No.1-5 of the example of this invention can obtain the outstanding performance which is not inferior even if tensile strength, fire retardancy, antibacterial, and any weighted solidity of a moisture absorption excel, although this invention person shortened sharply pH adjustment and the metal salt processing time compared with example No. of comparison6-7 proposed previously.

[0037] Example Oily medicine processing and dryness processing were performed for three sorts of pH buffer nature hygroscopicity fiber of the example of this invention (fiber No.1, No.4) created in the two examples 1, and the example of comparison (fiber No.6), and the 1.8 denier x48mm product raw cotton was obtained. According to the conventional method, cotton-mixing, a card, drawing, a roving, and fine spinning were performed for these product raw cottons, and the thread of the 1/52-meter yarn count and number of twists 830 T/M was created. Next, eyes are these thread at the smooth knitting machine of 20 gages 200*20 g/m² The knitting fabric sample of A to F shown in Table 3 was created. Subsequently, ***** was carried out for these sample knitting fabric by H₂O₂ / NaOH (pH=9 or 80-degree-Cx 60 minutes).

[0038]

[Table 3]

表 3

例	混紡率%	織地 サンプル No.	紡績加工 白粉発生	晒染色 染液漏り
本発明例	織維 No.1 / A n = 100 / 0	A	認めず	極僅か
本発明例	織維 No.4 / A n = 100 / 0	B	認めず	極僅か
本発明例	織維 No.1 / A n = 30 / 70	C	認めず	認めず
本発明例	織維 No.4 / C o = 30 / 70	D	認めず	認めず
比較例	織維 No.6 / A n = 100 / 0	E	あり	多い
比較例	織維 No.6 / A n = 30 / 70	F	少しあり	やや多い

A n : アクリル織維エクスラン K8-1.5 d x 51mm

C o : 木綿 コーマ

[0039] the example of this invention (fiber No.1, No.4) -- spinning -- knitting -- dyeing -- at any process, although there was also no problem on processing, the face powder was accepted at the card process and the fine-spinning process, and, as for the example of comparison (fiber No.6), many muddiness of ***** was accepted further This is considered because the unreacted calcium hydroxide remained inside a fiber front face and fiber in spite of having spent many hours on pH adjustment and metal hydroxide processing.

[0040] The result of the moisture absorption of sample knitting fabric A-F after *****, antibacterial, an antielectricity characteristic, and an anti-pill nature examination is shown in Table 4. It turns out that each sample knitting fabric A-B of the example of this invention shows the outstanding property, and the practical use effect shows sufficient property also in sample knitting fabric C-D of ** 30%. This will be carrying out metal salt processing, and will be because it reacted to homogeneity to the interior of fiber and endurance improved remarkably, after metal salt processing adjusts to pH 4.0-7.0 and uses a part of carboxyl group as a salt type. Although this invention person is maintaining target practicality ability even if it sets to sample knitting fabric E-F of the example of comparison, the point that there are restrictions in respect of processing is a problem.

[0041]

[Table 4]

表 4

例	編地 サンプル No.	抗菌性 S E K 菌数増減値差	20°C65%RH 吸湿率 (%)	20°C40%RH 半減期 (秒)	ICI 5Br 抗ピル性 (級)
本発明例	A	2.1	31.2	1.0	5
本発明例	B	2.2	27.6	1.3	5
本発明例	C	1.9	10.2	12	3
本発明例	D	1.8	8.7	14	3
比較例	E	2.0	25.9	2.2	5
比較例	F	1.8	7.9	18	3.5

[0042]

[Effect of the Invention] A means to manufacture industrially advantageously pH buffer nature hygroscopicity acrylic fiber and this fiber which the fiber physical properties which are satisfactory practically are maintained, and the saturation moisture absorption under 20 degree-Cx65RH has 15 - 35%, and have fire retardancy, antibacterial, an antielectricity characteristic, and anti-pill nature by this invention can be offered. pH buffer nature hygroscopicity acrylic fiber of this invention has itself in weak-acid nature, and is excellent in the acid from the external world, and the capacity maintained also to the attack of alkali at pH five to 7 within the limits. Moreover, specifically, a LOI display shows 24 or more fire retardancy, antibacterial exceeds a reference value 1.6 with the number increase-and-decrease of SEK bacilli difference of a value, anti-pill nature exceeds the 3rd class in the knitting fabric of ** 30% by the ICI method, and an antielectricity characteristic has many remarkable performances compared with the conventional synthetic fiber and the conventional natural fiber that the half-life under 20 degree-Cx40RH is less than 15 seconds in the knitting fabric of ** 30%. Furthermore, since various forms, such as a nonwoven fabric, knitting, and textiles, can be processed, a garments field is begun and it is widely used for all use fields, such as life materials and industrial materials.

[Translation done.]

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to pH buffer nature hygroscopicity acrylic fiber which has the function to hold pH of the water in contact with fiber to the weak-acid nature (only henceforth weak-acid nature) of pH 5-7, and has 15 - 35% of moisture absorption under 20-degree-C65%RH, and its manufacture method.

[0002]

[Description of the Prior Art] Although maintained at weak-acid nature in the normal state by the lactic acid secreted, by alkalinization of the acid rain accompanying environmental destruction in recent years, and the clothes by wash, the range with normal pH of the skin was surpassed and, as for people's skin, this has harmed the healthy skin. In order to maintain pH of the skin at weak-acid nature, while clothes neutralize the acid and alkali from the outside, it is desirable for the fibrin material in contact with the skin itself to be weak-acid nature. There is a thing to which the protein which has the isoelectric point in weak-acid nature was made to adhere by post processing to textiles as a method of replying to such a request. However, since this method was making pH buffer nature matter adhere to textiles by post processing, it was not what fills the demand of hygroscopicity has the fault which cannot process various kinds of forms easily, and increasing as social needs recently, fire retardancy, antibacterial, an antielectricity characteristic, and anti-pill nature.

[0003]

[Problem(s) to be Solved by the Invention] this invention person constructs a bridge by hydrazine processing in an acrylic fiber by Japanese Patent Application No. 6-36597, in order to cancel the trouble of such conventional technology. Subsequently, perform hydrolysis processing, and although pH buffer nature fiber characterized by changing the part into a metal salt type with a metal hydroxide after changing the generated carboxyl group into an acid type and its manufacture method were proposed When it is necessary to add small quantity every and a metal hydroxide addition is industrially manufactured since it is hard to react to homogeneity to the interior in case the swelling of fiber changes into a metal salt type small, when a carboxyl group is an acid type, time seriously This thing, Since a metal salt is mostly distributed over the surface section, when dyeing and finishing pH buffer nature fiber manufactured by the method, the thing for which it has a fault in endurance, such as a metal salt being omitted in high dyeing of especially dye liquor pH, and dye liquor polluting, and adhering to a stain riser product at powder, became clear.

[0004] this invention is originated in view of the present condition of this conventional technology, and the place made into the purpose is [pH buffer capacity of weak-acid nature is large, and] durable, and it has 15 - 35% of moisture absorption under 20-degree-C65%RH, and has various functions of the upper fire retardancy, antibacterial, an antielectricity characteristic, and anti-pill nature -- it is in pH buffer nature hygroscopicity acrylic fiber and its thing [offering the advantageous manufacture method industrially]

[0005]

[Means for Solving the Problem] this invention person resulted in completion of this invention, as a result of inquiring wholeheartedly, in order to attain the above-mentioned purpose. Namely, this invention is a bridge formation acrylic fiber whose increase in the nitrogen content by hydrazine bridge formation is 1.0 - 8.0 % of the weight. To a part of residual nitrile group, the carboxyl group of 2.5 - 4.5 meq/g The amide group is introduced into the remainder and a part of this carboxyl group sets to pH 4.0-7.0. The nitrate of calcium, Mg, and aluminum, It is the metal salt type which added and changed one sort or two sorts or more of metal salts chosen from a hydrochloride, a sulfate, and phosphate, and is pH buffer nature hygroscopicity acrylic fiber characterized by the equivalent ratio (metal pair H) being in the range of 1.0 to 1.5 to 4.0 to 1.0. Moreover, this invention introduces a crosslinking bond into an acrylic fiber by hydrazine processing, and the increase in a nitrogen content is adjusted to 1.0 - 8.0% of the weight of within the limits. A carboxyl group is introduced into 2.5 - 4.5 meq/g of the amount of nitrile groups which remains by the adding-water decomposition reaction, and an amide group is introduced into the remainder. at the time of acidolysis At the time of alkali hydrolysis with one sort or two sorts or more of hydroxides chosen from Li, Na, and K After one sort or two sorts or more of acids chosen from a sulfuric acid, a hydrochloric acid, a nitric acid, and phosphoric acid adjusting to pH 4.0-7.0 and using a part of carboxyl group as a salt type, It is the manufacture method of pH buffer nature hygroscopicity acrylic fiber characterized by adding one sort or two sorts or more of metal salts chosen from the nitrate of calcium, Mg, and aluminum as an indispensable component, a hydrochloride, a sulfate, and phosphate, and changing a part into a metal salt type.

[0006] Hereafter, this invention is explained in full detail. First, it may be fiber formed of AN system polymer which contains acrylonitrile (henceforth AN) 50% of the weight or more preferably 40% of the weight or more as the start acrylic fiber, and the